Oxidation of Fe Studied by PAC and Mossbauer Spectroscopy

I. 8. Oxidation of Fe Studied by PAC and Mössbauer Spectroscopy

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Introduction

Although Fe is one of the most technologically important materials, it is well known that it deteriorates during in use in an ambient atmosphere unless properly coated. This is due to the oxidation of Fe or steels by oxygen in the atmosphere. Also Fe oxides are utilized to fabricate electronics devices as storage media because of their unique magnetic properties. So the studies of Fe oxidation process or the properties of the oxcides are one important subject in materials science as well as in solid state physics.

In the present experiment, PAC as well as Mössbauer spectroscopy (CEMS) were performed to study the oxidation process of pure Fe or the magnetic properties of the resulting oxcides.

Experimental

PAC: The PAC probe ^{111}In was implanted to an Fe specimen at the energy of 40keV to the activity of several 10μCi. The specimen was annealed in an UHV at 400C to anneal out the damages due to the implantation. Subsequently, an oxidation procedure (500C×30min, 5×10^{-1} Torr air. Treatment I) was given to the specimen. After measuring the PAC spectrum, the specimen was given two annealing treatments(500C× 30min, 10^{-7} Torr UHV, Treatment II: an additional 6 hrs at 500C in UHV,Treatment III: and 30min at 600C in UHV,Treatment IV) for further PAC spectroscopies. As will be shown later, these annealing tveutments mentsin a vacuum are crucial to obtain a good PAC spectrum for the present Fe oxides using ^{111}In as the probe. The PAC spectroscopy was performed at RT in a three detectors mode with and without a vertical magnetic field.

CEMS: Almost the same oxidation treatments were given to an Fe foil (^{57}Fe enriched)for CEMS. The purpose of CEMS is to identify the species of oxides formed during the treatments. The use of the enriched foil is to obtain a high S/N ratio spectrum within a reasonably short time.

Results and Discussion

Fig.1 shows the results of the PAC spectrum measurements for Fe given the treatments described above. After the Treatment I, the spectrum shows a precession pattern with a very small amplitude (comparable with that in pure Fe). However, the amplitude becomes quite large after the treatment II and grows further after the Treatment III or IV. Since the period of the precession is 36 ns for the null external magnetic field(H=0) measurement and about 3 times longer than that in pure Fe (11.2ns), ^{111}In should be in an oxide phase and not in Fe host. The precession period becomes half upon the application of the vertical magnetic field and so the coupling of ^{111}In in the oxide is magnetic and not quadrupolar. This effect of the external magnetic field is in accord with a theoretical study[1] and also with the experimental results in Ni[2].

In order to examine what kind of oxides are formed after each treatments, CEMS were performed for Fe given the same treatments as the PAC specimen. Fig. 2 shows the results and reveals that γ Fe_2O_3 (mag-hematite) is formed after the Treatment I and Fe_3O_4 (magnetite) after Treatment II. These identifications are confirmed by (1) additional MS on Fe_2O_3 or Fe_3O_4 powders obtained as chemicals in the present and (2) other MS results on Fe oxides[3].

So we can conclude that the amplitude of PAC spectrum is quite large in Fe_3O_4 but not in Fe_2O_3. Since the amplitude of the PAC precession pattern stays constant up to 350ns and shows no dumping at RT, the frequency (or similarly, the magnitude of the hyperfine field) has only one value in Fe_3O_4 for ^{111}In. This shows a discrepancy from the result of CEMS since it shows that there are two magnetically different sites (Fe_3O_4-I and -II as shown in Fig.2) for ^{57}Fe. So the possibilities are: (1) different from the ^{57}Fe probe ,only one site is occupied by the ^{111}In probe or (2) both sites are occupied by ^{111}In but with exactly the same magnitude of the hyperfine field. Here we assume that the ^{111}In ions occupy the same sites with Fe ions and not that of O ions. Further experiments are now in progress to solve the apparent discrepancy between CEMS and PAC results.

In a previous paper where a result of an attempt to prepare a ^{111}In-Fe specimen by a diffusion method has been reported[4], a precession pattern with the period of 1/3 of that in Fe was found in a specimen annealed for several 10hrs in H_2. This has been interpreted by the present author as due to ^{111}In adsorbed on the surface. In the present light of oxidation experiments, however, the result should be interpreted as that an oxide layer was formed even in the H_2 treatment thus giving rise to the 1/3 precession pattern.

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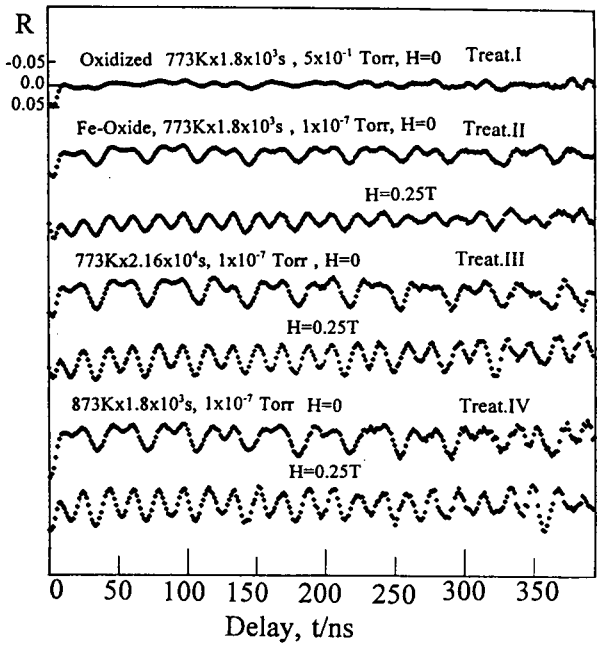

Fig. 1. PAC spectra for Fe during the oxidation treatments.

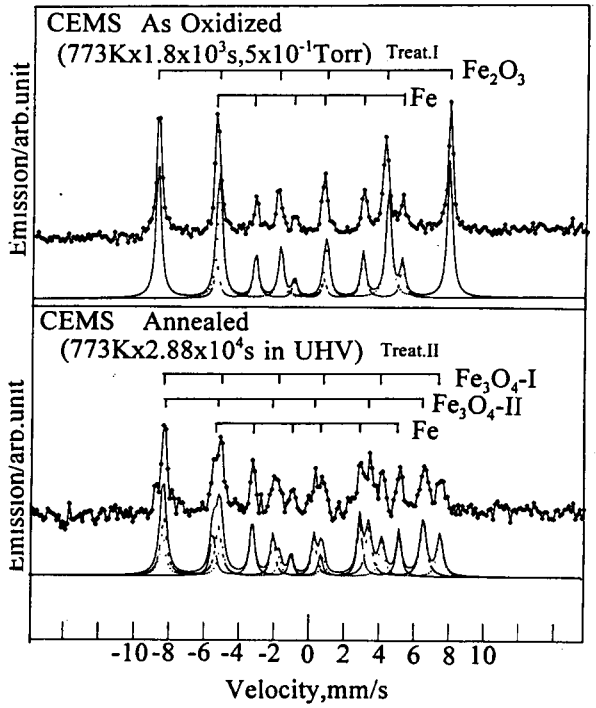

Fig. 2. CEMS spectra for Fe during the oxidation treatments. Data (symbols) and calculated (lower lines).